A molecular thermometer based on long-lived emission from platinum octaethyl porphyrin

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A highly sensitive molecular thermometer based on platinum octaethyl porphyrin, which can be employed in a range of environments, is presented. The thermal activation of the emission spectrum results in a change in emission intensity by an order of magnitude over a temperature range of 45 K about room temperature. The long-lived molecular emission enables the characterization of thermal effects in common conjugated polymers under optical excitation. It is found that optical heating does not contribute to material breakdown, which is governed by photo-oxidation. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1509115]

The miniaturization of nanoscale electronic and optoelectronic devices has advanced over the past years in great strides and has recently led to the demonstration of truly molecular devices.[1] Inevitably, thermal effects will become increasingly important as electronic components are scaled down in size. This is particularly relevant in the case of organic semiconductors, which often have low mobilities, and may be a source of long-term operating instabilities,[1] but is also a known problem in inorganic semiconductor miniaturization. It is therefore imperative to develop tools to characterize local and global heating effects in nanostructured devices. There has recently been interest in the development of nanothermometers based on carbon nanotubes,[2] however these devices are still too large to image thermal effects on the molecular scale. Fortunately, some molecules are known to exhibit temperature dependent spectral changes. Fluorescence ratio and fluorescence lifetime based thermal imaging as well as fluorescence upconversion are the most promising techniques to access thermal effects on a molecular scale,[3-9] although changes in excited state absorption have also been used.[10,11] Most molecular thermometers, however, are very sensitive to the host environment and operate only in solution or certain crystal lattices. It is demonstrated here that a popular organic semiconductor, platinum octaethyl porphyrin, can act as a highly sensitive molecular thermometer. In an example application the effect of sample heating on the chemical degradation of a conjugated polymer upon photoexcitation is investigated.

The porphyrin studied is 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP, obtained from Porphyrin Products Inc.) and is shown in Fig. 1. It has been studied extensively[12] and has been shown to yield highly efficient organic light-emitting diodes (LEDs).[13,14] The emission spectrum is dominated by a strong red band at 650 nm, which has previously been assigned to the triplet $T(0,0)$ level.[12] In the following experiment the luminescence was excited by an 80 MHz mode-locked frequency-doubled titanium–sapphire laser operating at 380 nm and was detected by a CCD spectrometer. The sample was mounted under helium atmosphere in a helium cryostat. By observing the luminescence from a PtOEP doped polystyrene film through a short-pass transmission filter, a further emission feature is observed with bands at 540 and 580 nm. Figure 1 shows the transmission spectrum of the filter used together with emission spectra recorded between 320 and 290 K. The feature at 540 nm, which is ~3 orders of magnitude weaker in intensity than the main $T(0,0)$ emission, is found to be strongly thermally activated. By correcting for the background and considering the ratio between the two emission features, an activation energy of 0.42 eV is obtained, as shown in Fig. 2. Around room temperature, this corresponds to an order of magnitude change in intensity over a range of 45 K. Using standard spectroscopic detection a sensitivity of better than 0.25 K is achievable, which could be dramatically improved by the use of lock-in techniques.

The origin of the band at 540 nm is not entirely clear, but it is noted that the thermal activation of 0.42 eV corresponds to the splitting between the $T(0,0)$ band and the weak band of 0.38 eV. This suggests that the 540 nm emission originates

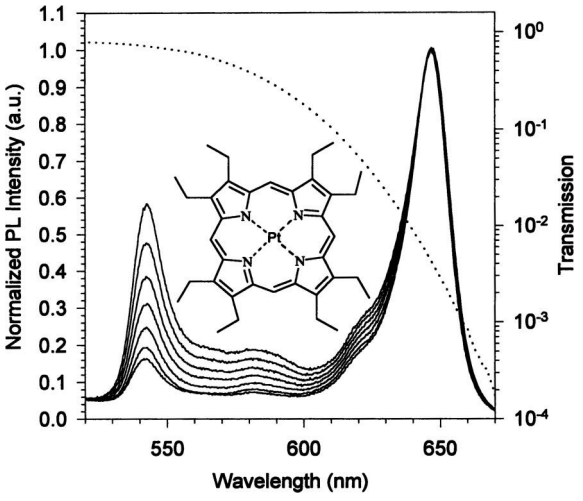

FIG. 1. PL spectra of PtOEP excited at 380 nm measured through a short wavelength pass filter at temperatures of 320, 315, 310, 305, 300, 295, and 290 K (from top to bottom). The spectra are normalized to the emission band at 650 nm. The transmission of the filter is also shown (dotted line). The inset shows the structure of PtOEP.

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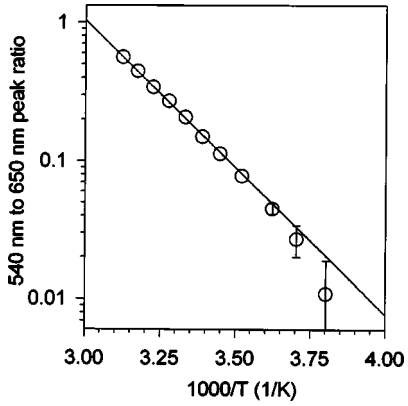

FIG. 2. Thermal activation of the 540 nm emission peak with respect to the 650 nm peak.

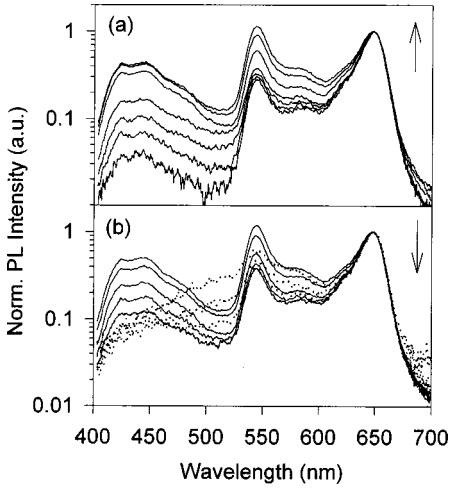

FIG. 3. Delayed PL spectra of a 10% by weight blend of PtOEP in PFO, measured in a 2 ns window 1.5 ns after excitation, normalized to the 650 nm band. (a) Laser power increasing from 0.1 to 11 mW (from bottom to top). (b) Laser power decreasing from 11 to 0.1 mW. The dotted lines show the spectra recorded at 0.1, 0.2, and 0.5 mW (relative fluorenone emission increasing with decreasing laser power).

from a "hot" level which is populated by the emission from the level responsible for the main phosphorescence. Weakly thermally activated bands, so called hot bands, have previously been observed in some fluorescent porphyrins in solution,[15,16] but not in strongly phosphorescent metalloporphyrins. The present observation is rather surprising, as internal conversion should compete strongly with phosphorescence from a higher lying triplet state and render hot band phosphorescence impossible. In contrast, the PtOEP singlet at 585 nm is known to have a very low quantum yield and to decay within 70 ps.[12] It is therefore hard to conceive that the 540 nm band originates either from a higher lying triplet or singlet state.

The feature at 540 nm is long lived on the time scale of tens of nanoseconds and hence allows temperature measurements to be made in materials with short-lived strong singlet emission by employing a gated detection technique. This is demonstrated in the following for a 10% by weight blend of PtOEP in the semiconducting conjugated polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO, obtained from American Dye Source Inc.), which is a blue-emitting polyfluorene derivative. Polyfluorenes are known to oxidize under certain conditions, leading to molecular fluorenone units on the backbone, which are characterized by a long-lived broad emission band centered at 530 nm.[17,18] It has been pointed out that this emission component is enhanced strongly and irreversibly upon heating of the sample.[19] It is also known that the emission component increases upon photo-oxidation under an intense UV lamp.[17,20] However, it is not known whether intense UV excitation actually leads to a temperature increase on the molecular level, catalyzing the chemical oxidation responsible for defect formation.

Using the molecular thermometer it is possible to measure the film temperature after excitation by a 200 fs UV laser pulse focused to $\sim 100\ \mu$m and to correlate this with the irreversible change in photo-oxidation. To do this the sample was held under a vacuum of 10^{-4} mbar and was prepared by spin coating from a fresh solution. Delayed emission spectra were recorded using a Hamamatsu streak camera synchronized to the 80 MHz repetition rate of the pump laser. Figure 3 shows delayed PL spectra of the PFO: PtOEP blend recorded 1.5 ns after excitation in a 2 ns time window. Figure 3(a) displays the change in the delayed spectra, normalized to the PtOEP $T(0,0)$ emission, as the laser power is increased from 100 μW to 11 mW. The delayed detection procedure is very sensitive to the long-lived fluorenone emission.[18] As the laser power is increased the intensity of the hot band increases. The broad emission band centered at 530 nm, the fluorenone emission also increases slightly, overlaying the PtOEP hot band. This arises due to an irreversible oxidation process which increases both with time and with excitation power. The delayed blue PFO backbone emission also increases due to the increased formation of long-lived emissive species at higher excitation intensities.[21] As the laser power is decreased again in Fig. 3(b), the hot band intensity decreases as well as the delayed PFO emission with respect to the PtOEP emission. The decrease in the fluorenone emission is, however, slower and at low excitation powers the fluorenone defect emission dominates the delayed PL spectrum [dotted lines in Fig. 3(b)]. This is because the newly formed fluorenone sites act as exciton traps in a similar way to the PtOEP sites, and therefore have the same activation channel. The spectra in Fig. 3 show relatively weak fluorenone emission. It was found, however, that different polyfluorene batches from different sources displayed vastly different fluorenone emission intensities in the delayed spectra. In the case of strong fluorenone emission (not shown) an irreversible increase in fluorenone emission with increasing laser power was observed with no increase in sample temperature.

Figure 4 shows the film temperature deduced from the peak ratio in the delayed PtOEP emission intensity in Fig. 3. Due to the contribution from defect emission created by photo-oxidation the hot band intensity is overestimated at low powers after decreasing the laser power again (open triangles). The delayed spectra were therefore corrected for the molecular fluorenone emission, yielding a corrected temperature (solid symbols). The film temperature clearly increases linearly by up to 25 K with increasing laser power, as would be expected. In order to check the correct operation of the thermometer a control experiment was performed at low laser power. Heating the film up by a given temperature inside

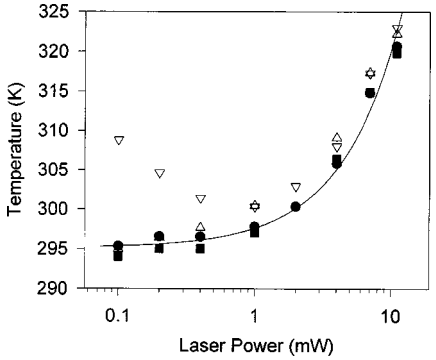

FIG. 4. Dependence of film temperature on laser power: power increasing (triangle up); power decreasing (triangle down); power increasing, emission corrected for defect band (solid square); power decreasing, emission corrected for defect band (solid circle). The line indicates a linear fit to the corrected data.

the cryostat yielded exactly the same change in peak ratio observed in Fig. 3 and expected from the thermal activation shown in Fig. 2. It should be noted that the fluorescence quantum yield of polyfluorenes is rather high, up to 60%, which explains in part the surprisingly low heating observed below 1 mW. It should also be noted that the temperature rise observed in the present case is in stark contrast to that observed in polyfluorene LEDs, which show a temperature rise of over 30 K.[22] As the excitation densities in LEDs are much lower than in the present pulsed optical excitation experiment it can be concluded that heat accumulation in LEDs arises mainly due to ohmic heating and nonradiative triplet exciton decay, rather than nonradiative decay of singlet excitations due to a nonunity fluorescence yield.

The present demonstration of the use of molecular thermometry to study the degradation of polyfluorenes shows that the creation of fluorenone exciton[17,18] and charge carrier[17,23] traps is purely photochemical in origin, rather than thermal. Thermally induced irreversible spectral changes[19] are most likely due to increased reaction rates, but evidently play no or little role in optical excitation. Long-term stability in high power optical devices such as lasers and amplifiers can therefore only be achieved by rigorous chemical purity, inhibiting the formation of oxidation sites, rather than elaborate thermal management. Besides allowing insight into photochemical processes, the molecular thermometer should also complement fluorescence quantum yield measurements allowing a characterization of nonradiative decay channels as well as thermalization processes of hot excitons.

In summary, a highly sensitive molecular thermometer has been demonstrated. It is envisaged that the combination with near field or confocal optical microsopy will allow the characterization of subtle thermal effects down to nanoscopic scales.

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